

# Electronic structure and magnetism of a ferromagnetic insulator $\text{Cs}_2\text{AgF}_4$ : explanation for a lilac colour and a prediction for the anisotropic $g$ factor

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Magnetic properties of stoichiometric  $\text{Cs}_2\text{AgF}_4$  have been calculated within a very strong correlation limit taking into account a low-symmetry crystal field and the intra-atomic spin-orbit coupling of the  $\text{Ag}^{2+}$  ion. We consistently explain the insulating ground state and the magnetic state revealing the spin gap of 2.6 meV below  $T_c$  of 14.9 K. A  $d-d$  excitation of 2.0-2.3 eV related to the  $t_{2g}-e_g$  promotion energy ( $=10Dq$ ) is a reason for the lilac colour of  $\text{Cs}_2\text{AgF}_4$ . Our approach can be experimentally verified by the measurement of the  $g$  factor ( $g_z=2.12$  and  $g_y=2.52$ ) and the absorption energy at 2.0-2.3 eV.

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## I. INTRODUCTION

$\text{Cs}_2\text{AgF}_4$  is a unique 4d ferromagnet<sup>1,2</sup> - the most of fluorides and oxides are antiferromagnetic. Despite that  $\text{Cs}_2\text{AgF}_4$  has already been synthesized 30 years ago<sup>2</sup> recently it draws attention<sup>3,4,5,6,7</sup> being regarded as an analog of  $\text{La}_2\text{CuO}_4$ , a maternal high-temperature superconductor. Thus it seems to be very good exemplary system for studying basic interactions in  $d$  fluorides and oxides.

$\text{Cs}_2\text{AgF}_4$ , when stoichiometric, is a good insulator. It is ferromagnetic below  $T_c$  of 14.9 K<sup>1</sup> or 13.95 K<sup>3</sup>. The macroscopic magnetisation, if recalculated per the formula unit, points to a moment of about  $0.8 \mu_B$ <sup>1</sup>. The paramagnetic susceptibility has been found to follow the Curie-Weiss law<sup>1</sup>. Already above 50 K there is a straight  $\chi^{-1}$  vs  $T$  line with  $\theta_{CW} = +30$  K.

The origin of the ferromagnetic state and the insulating state is recently of a large theoretical discussion in Phys. Rev. journals<sup>3,4,5,6,7,8</sup>. As far as the ferromagnetic state is discussed another fluoride ferromagnetic compound  $\text{K}_2\text{CuF}_4$  has been recalled. They both have similar structure based on the  $\text{K}_2\text{NiF}_4$  structure. Kasinathan *et al.*<sup>4</sup> have explained, within density-functional theory (DFT), the ferromagnetic structure as originating from the substantial Ag-F covalency. But this covalency causes simultaneously the incorrect itinerant, not insulating, ground state and a substantial magnetic moment on the fluorine ions. Dai *et al.*<sup>5</sup> suggested that the ferromagnetism originates from the spin polarization induced by the  $d_{z^2}-p-d_{x^2-y^2}$  orbital interaction through the Ag-F-Ag bridges. In Refs<sup>4,5</sup> authors dealt with the tetragonal structure and obtained a half-metallic solution in the ferromagnetic state - this half-metallic solution, being essential for their explanation of the ferromagnetism in  $\text{Cs}_2\text{AgF}_4$ , disagrees with the insulating ground state observed experimentally. In following studies Kan *et al.*<sup>6</sup>, performing pseudopotential DFT calculations for the or-

thorhombic lattice, have obtained an orbitally ordered solution but with unphysically large in-plane and out-of-plane magnetic coupling strengths. More recently, Hao *et al.*<sup>7</sup> and Wu and Khomskii<sup>8</sup>, using DFT total-energy calculations, have found that the orthorhombic lattice is more energetically stable than the undistorted tetragonal lattice. Moreover they theoretically found that this inherent lattice distortion is accompanied by the Ag 4d-orbital ordering and this orbital ordering accounts for the observed ferromagnetism of  $\text{Cs}_2\text{AgF}_4$  similarly like for an isoelectronic and isostructural compound,  $\text{K}_2\text{CuF}_4$ . Wu and Khomskii found, within the GGA+U calculations with  $U = 3$  eV, that " $\text{Cs}_2\text{AgF}_4$  is stabilized in an insulating orthorhombic phase rather than in a metallic tetragonal phase" and that "the ground state is orbitally ordered ferromagnetic state". This orbitally ordered ferromagnetic ground state is realized by the alternative hole occupation in the  $x^2 - z^2/y^2 - z^2$  orbitals.

Analyzing this recent theoretical work of Wu and Khomskii we would like to put attention to the following outcomes:

- 1) the orthorhombic distortion is necessary to get insulating ground state - within the GGA approach with  $U=0$  there is a small gap of 0.2 eV only; this gap increases to 1 eV for an expected  $U$  value of 3 eV;
- 2) the insulating gap of 0.2 eV, as well as 1 eV, is formed within **the spin-polarized**  $x^2 - z^2$  state (Fig. 4<sup>8</sup>);
- 3) a size of the spin splitting is very large - in case of the  $x^2 - z^2$  state the spin splitting amounts to 0.75 eV ( $U=0$ , see Fig. 1) and it increases to 1.5 eV for the final calculations with  $U=3$  eV (Fig. 4<sup>8</sup>).
- 4) there is a relatively strong spin polarization of the F atoms - the local spin moment of each apical F ( $F_1$ ) amounts to  $0.099 \mu_B$  and of each planar F ( $F_2$ ) amounts to  $0.097 \mu_B$ . Thus all fluorine atoms contribute by  $0.392 \mu_B$  per formulae unit to the resultant magnetisation. It is 40 % of the calculated total magnetisation, of 0.992

$\mu_B/\text{f.u.}$ .

5) there is a relatively small magnetic moment of Ag, of  $0.600 \mu_B$  only; thanks the large F-atom contribution the resultant magnetisation, being  $0.992 \mu_B$ , becomes close to the integer  $1 \mu_B$ , expected for a  $S = 1/2$  spin.

The aim of this paper is to present results of calculations of properties of  $\text{Cs}_2\text{AgF}_4$  within the very strong-correlation limit.

## II. THEORETICAL OUTLINE

The very strong-correlation limit has a lot in common with the ionic model and the many-electron crystal-field model which we consider to be to a large extent relevant to the reality of oxides and fluorides. We would like to note that we employ the many-electron version of the crystal-field theory instead of the one-electron version mentioned in Refs<sup>4,5,6,7,8</sup>. Our electronic structure is different from those obtained in Refs<sup>4,5,6,7,8</sup> despite that energies of  $e_g$  and  $t_{2g}$  states are discussed. According to us, and in contrary to the above-mentioned papers<sup>4,5,6,7,8</sup>, strong correlations are realized i) by the relevant charge transfer during the formation of the compound which leads to the charge distribution  $\text{Cs}_2^{1+}\text{Ag}^{2+}\text{F}_4^{1-}$  and ii) by strong correlations among nine  $d$  electrons of the  $\text{Ag}^{2+}$  ion. These strong intra-atomic correlations among nine  $d$  electrons assure that they should be considered as the whole  $4d^9$  system being described by quantum numbers  $L=2$  and  $S=1/2$  (term  $^2D$ ). In  $\text{Cs}_2\text{AgF}_4$  the octahedral fluorine surroundings splits 10 states for the lowest four ( $^2E_g$ ) and higher six states ( $^2T_{2g}$ ) (Fig. 1b). The compressed tetragonal distortion occurring in  $\text{Cs}_2\text{AgF}_4$  causes a splitting of the lowest quartet for two Kramers doublets (Fig. 1d). The longest bond along y-axis occurring in  $\text{Cs}_2\text{AgF}_4$  enlarges only this splitting (Fig. 1e) as the Kramers doublet cannot be split by any lattice distortion. The Kramers doublet is only split by a magnetic field, external or internal. We have calculated that the  $\text{Ag}^{2+}$  moment experiences internal molecular field of 17.4 T (at  $T = 0$  K).

## III. RESULTS AND DISCUSSION

We accept experimental lattice parameters at  $T = 293$  K, according to Ref.<sup>1</sup>, cited by<sup>8</sup>:  $a_o = 643.5$  pm,  $b_o = 643.9$  pm and  $c_o = 14.150$  pm and the respective Ag-F lengths: in-plane 216.8 pm (Ag-F<sub>2</sub>(a)), 238.3 pm (Ag-F<sub>2</sub>(b)) and the apical bond 217.2 pm (Ag-F<sub>1</sub>(c)).

This situation in  $\text{Cs}_2\text{AgF}_4$  we account for by crystal-field parameters (z along the c axis) of  $\text{Cs}_2\text{AgF}_4$ :  $B_4 = -18$  meV (octupolar charge interactions predominantly due to the octahedron of fluorines, minus sign is related to the negative charge at the F ions),  $B_2^0 = +2$  meV (quadrupolar (axial term) charge interactions, positive sign corresponds to the compression along z-axis);  $B_2^2 = -7$  meV (quadrupolar (planar term) charge interactions,

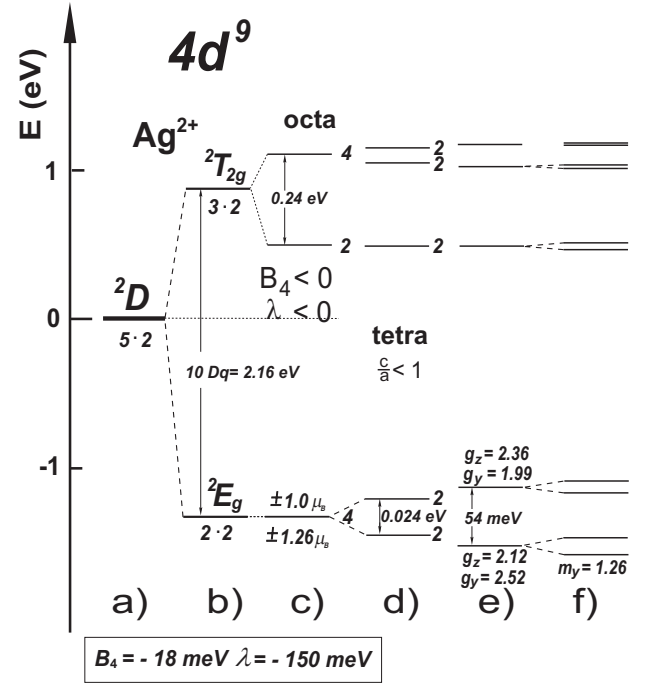


FIG. 1: The calculated fine electronic structure of the  $4d^9$  electronic system ( $\text{Ag}^{2+}$ ,  $\text{Cu}^{2+}(3d^9)$  ions) in the paramagnetic state under the action of the crystal field and spin-orbit interactions: a) the 10-fold degenerated  $^2D$  term realized in the absence of the CEF and the s-o interactions; b) the splitting of the  $^2D$  term by the octahedral CEF surrounding  $B_4 = -18$  meV ( $\lambda_{s-o} = 0$ ) yielding the  $^2E_g$  cubic subterm as the ground state and  $10Dq = 2.16$  eV; c) the effect of the spin-orbit ( $\lambda_{s-o} = -150$  meV) for the octahedral CEF states causing a splitting of the higher  $^2T_{2g}$  cubic subterm as the ground state and the associated magnetic moments are shown; d) the splitting due to the compressed tetragonal off-octahedral distortion of  $B_2^0 = +2$  meV ( $c/a < 1$  apical fluorines become closer); e) the splitting due to the in-plane off-tetragonal distortion (elongation along y-axis) of  $B_2^2 = -7$  meV; f) - the splitting in the magnetic state. Figs c, d, e and f are not to the left hand energy scale.

negative sign corresponds to the elongation along y-axis). We take also into account the intra-atomic spin-orbit coupling  $\lambda_{s-o}$  of  $-150$  meV - its effect is not visible in the splitting of the  $^2E_g$  subterm (Fig. 1c) but the spin-orbit coupling affects the eigenfunctions of the  $^2E_g$  subterm and its magnetic characteristics. As a consequence the moment of the ground-state doublet is not any more the integer  $1 \mu_B$  but  $\pm 1.26 \mu_B$  for the present calculations (Fig. 1e). The detailed eigenfunctions, the energy states, and the magnetic moment can be calculated like we have demonstrated for many compounds ( $\text{Fe}^{2+}$  ion in  $\text{FeBr}_2$ <sup>9</sup> and  $\text{FeO}$ <sup>10</sup>,  $\text{Co}^{3+}$  in  $\text{LaCoO}_3$ <sup>11</sup>,  $\text{Ti}^{3+}$  in  $\text{YTiO}_3$ <sup>12</sup>,  $\text{Co}^{2+}$  in  $\text{CoO}$  or  $\text{Ni}^{2+}$  in  $\text{NiO}$ <sup>13</sup>) both in the paramagnetic state and in the magnetically-ordered state.

The respective Hamiltonian is considered in the LS space that is the 10 dimensional spin-orbital space  $|LSL_zS_z\rangle$ . Despite of the relative weakness of the s-o

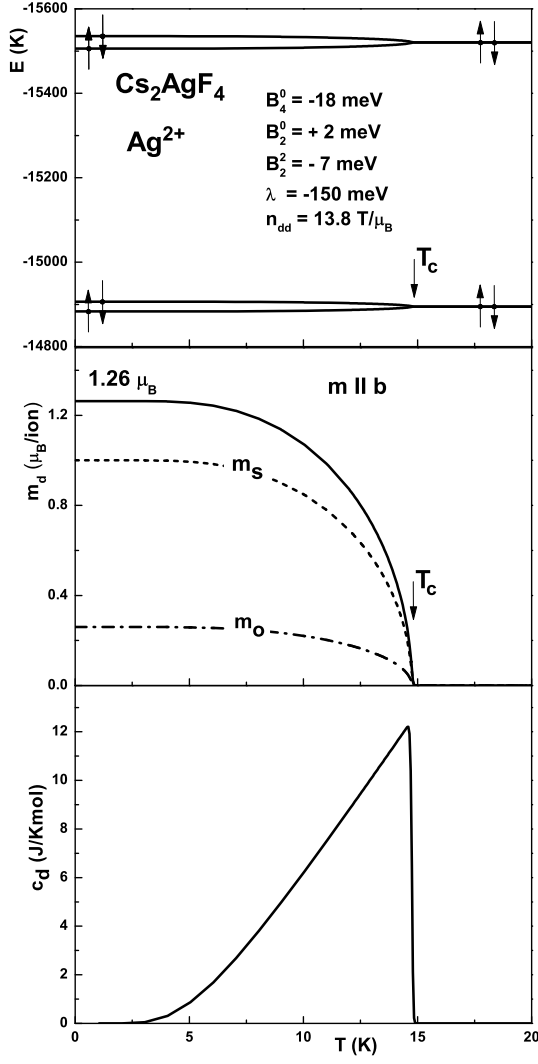


FIG. 2: The calculated temperature dependence of some properties of  $\text{Cs}_2\text{AgF}_4$ . a) the temperature dependence of the two lowest states ( $^2E_g$  states) of the  $\text{Ag}^{2+}$ -ion in  $\text{Cs}_2\text{AgF}_4$  in the magnetically-ordered state below  $T_c$  of 14.9 K; in the paramagnetic state the electronic structure is temperature independent unless we do consider a changing of the CEF parameters, for instance, due to the thermal lattice expansion. The used parameters:  $B_4^0 = -18$  meV,  $B_2^0 = +2$  meV,  $B_2^2 = -7$  meV,  $\lambda_{s-o} = -150$  meV and  $n_{d-d} = 13.8$  T/ $\mu_B$ . In the ferromagnetic state the Kramers doublets become split. Excited states are at 2.06, 2.28 and 2.30 eV. (b) the temperature dependence of the  $\text{Ag}^{2+}$ -ion magnetic moment in  $\text{Cs}_2\text{AgF}_4$ . At 0 K the total moment  $m_{Ag}$  of  $1.26 \mu_B$  is built up from the orbital  $m_o$  and spin  $m_s$  moment of 0.26 and  $1.00 \mu_B$ , respectively. (c) The calculated temperature dependence of the  $4d$  contribution  $c_d(T)$  to the heat capacity of  $\text{Cs}_2\text{AgF}_4$ . The  $\lambda$ -type peak marks  $T_c$ .

coupling for the  $d$  ions in comparison to the strength of the crystal-field interactions we have performed direct calculations treating all terms in the Hamiltonian on the same footing. Due to the spin-orbit coupling the involved functions are not any more the pure cubic  $e_g$  ( $x^2 - y^2$  or  $3z^2 - r^2$ ) and  $t_{2g}$  states.

An analysis of the effect of the sign of the tetragonal off-octahedral distortion leads to a conclusion that for the elongation along  $z$ -axis ( $c/a > 1$ ) the magnetic moments order along the tetragonal axis. In case of the compression ( $c/a < 1$ ) the moments are confined to the tetragonal plane. But then an in-plane distortion has to occur in order to remove the in-plane frustration - thanks this distortion a specific direction in the plane can be selected. Again the moment is directed along the most elongated bond - exactly as it is in case of  $\text{Cs}_2\text{AgF}_4$ , where the ordered moment lies along the  $y$  direction having the biggest length. The  $B_2^2$  parameter is related to the bond difference in the  $a - b$  plane.

The calculated charge-formed ground-state has  $\langle S_z \rangle = \pm 1.00$ ,  $\langle L_z \rangle = \pm 0.26$  and the quadrupolar moment  $Q = +5.97$ . The moments  $m_y = \pm 1.26 \mu_B$  cancel each other in the paramagnetic state, Fig. 2a. They reveal themselves in the magnetic state when the Kramers-doublet ground-state function becomes polarized because a molecular field is self-consistently settled down.

Below  $T_c$  there opens, as is seen in Fig. 2a, a spin-like gap that amounts at  $T = 0$  K to 2.6 meV. The spin-like gap is associated with the splitting of the Kramers doublet ground state in the ferromagnetic state. The magnetic ground state  $\psi_{GS+}$  has  $\langle S_z \rangle = 1.00$ ,  $\langle L_z \rangle = +0.26$  and the resultant moment of  $1.26 \mu_B$ . The appearance of the magnetic state is calculated self-consistently. It appears at the instability temperature ( $T_c$ ) in the temperature dependence of the CEF paramagnetic susceptibility when

$$\chi_{CF}^{-1}(T_c) = n_{d-d}$$

where  $n_{d-d}$  is the molecular-field coefficient accounting spin-dependent interactions. The ordering temperature of 14.9 K yields  $n_{d-d} = 13.8$  T/ $\mu_B$  ( $= 9.27$  K/ $\mu_B^2$ ) for all magnetic interactions of the given Ag-moment with its magnetic neighbours. The Ag moment experiences at  $T = 0$  K a field of 17.4 T.

From the calculated free energy  $F(T)$  we calculate all thermodynamics like temperature dependence of the magnetic moment, of the additional heat capacity  $c_d$ , of the paramagnetic susceptibility  $\chi_d$ , of the  $4d$ -shell quadrupolar moment and many other properties similarly to those performed for  $\text{FeBr}_2^9$ ,  $\text{CoO}^{13}$  and  $\text{YTiO}_3^{12}$ .

Comparing our results with those of the Wu-Khomski's approach 1) we claim that the distortion is not necessary for  $\text{Cs}_2\text{AgF}_4$  to be insulator - it is unphysical to think that so small effect can produce so drastic change of electrical properties, 2) we question an understanding that the insulating gap occurs within the **spin-polarized**  $x^2 - z^2$  state - it would mean that  $\text{Cs}_2\text{AgF}_4$  would be insulating only in the magnetically-ordered state - although we do not have experimental results at hands we believe that  $\text{Cs}_2\text{AgF}_4$  is insulating both in the ferromagnetic state as well in the paramagnetic state above 14.9 K, 3) the spin splitting of 2.6 meV is more physically realistic for a compound with  $T_c$  of 14.9 K than 1.5 eV<sup>8</sup> corresponding to the thermal energy of 17400 K.

#### IV. CONCLUSIONS

We have calculated consistently a value of the magnetic moment of  $1.26 \mu_B$  in  $\text{Cs}_2\text{AgF}_4$  and its direction, along the  $y$  axis in the orthorhombic structure originating from the tetragonal  $\text{K}_2\text{NiF}_4$ -type structure. We have derived the spin and orbital moment and found that the orbital magnetic moment cannot be ignored in any discussion of magnetic and electronic properties of any  $d$ -containing compound. It confirms the importance of the spin-orbit coupling which entangles the spin and orbital degree of freedom. We have derived the electronic structure both in the paramagnetic and ferromagnetic state showing that this structure is only slightly modified by the formation of the magnetic state. The respective spin-polarization energy is only  $1.3 \text{ meV/f.u.}$  - it is almost 1000 times less than regarded in the recent theoretical papers. We derive the strength of the octupolar charge interactions at the Ag site to be  $2.16 \text{ eV}$  - it determines

the  $t_{2g}-e_g$  promotion energy ( $=10Dq$ ). This  $d-d$  excitation is a reason for the lilac colour<sup>1</sup> of  $\text{Cs}_2\text{AgF}_4$ . In our understanding the insulating gap is much larger than  $2.16 \text{ eV}$ , say  $4-5 \text{ eV}$ , and  $\text{Cs}_2\text{AgF}_4$  is insulating both in the tetragonal and the orthorhombic phase. Our results are important because the  $t_{2g}-e_g$  and spin-polarization energy are the basic ingredient for any theory dealing with  $d$  electron systems. These studies prove that magnetic properties of  $\text{Cs}_2\text{AgF}_4$  are predominantly determined by the atomic-scale lattice distortions, crystal-field and the spin-orbit coupling of the  $\text{Ag}^{2+}$  ions, whereas charge fluctuations are of the minor importance. An interplay of the spin-orbit coupling, lattice distortions and the magnetic order is very subtle and involves rather small energies, smaller than  $5 \text{ meV}$  making theoretical studies difficult. We point out that all discussed by us parameters are physical measurable parameters. Our approach can be experimentally verified by the measurement of the  $g$  factor and the energy absorption at  $2.0-2.3 \text{ eV}$ .

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